

A comment on “Interlayer interactions in graphites” [Chen et al., Sci. Rep. 3, 3046 (2013)]

Tim Gould

*Queensland Micro and Nano Technology Centre,
Griffith University, Nathan, Queensland 4111, Australia*

Tomáš Bučko

*Comenius University in Bratislava,
Faculty of Natural Sciences, Slovakia, Theoretical Chemistry*

Sébastien Lebègue

*Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM2,
UMR CNRS 7036) Institut Jean Barriol, Université de Lorraine,
BP 239, Boulevard des Aiguillettes 54506 Vandoeuvre-lès-Nancy, France*

Abstract

Determining the material properties of layered systems like graphite and bigraphene from *ab initio* calculations is very difficult. This is mostly due to the complex van der Waals forces which help bind the layers. Recently, Chen *et al.*[1] reported a novel approach for extracting geometry dependent energetic properties of general, layered graphitic systems from periodic graphite calculations on AA, AB and ABC graphite. Unfortunately, their analysis suffered from a number of technical and theoretical flaws which make their results unreliable for predicting energetic properties. We propose that their conclusions in this regard should be reassessed, or reanalysed using more appropriate van der Waals theory[2–5].

TABLE I. Geometrically determined differences in the potential energy minima of AB graphite in meV/Atom (for exfoliation: meV/Surface Atom).

	Chen <i>et. al</i> [1]	Gould <i>et. al</i> [9]	Björkman <i>et. al</i> [10]
$E_{\text{Bigraphene}} - E_{\text{Graphite}}$	2.0	4.1	–
$E_{\text{Bigraphene}} - E_{\text{Exfoliation}}$	2.0	6.5	6.5

To determine graphitic material properties, Chen *et al.*[1] (CTPDC) utilise a number of recent developments in *ab initio* theory in combination with a Möbius inversion method. While we believe their use of Möbius inversion is scientifically justified, at least within the limits of additive van der Waals theory[3, 6, 7], the *ab initio* and analytic inputs used are less well justified and will make their energetic predictions unreliable. Indeed their application of Grimme’s DFT-D2 method[8], and their fitting and theoretical conclusions all seem to have fundamental flaws. Without good theoretical input, the Möbius inversion method cannot be expected to produce appropriate quantitative conclusions, and we show that this is indeed the case.

In their analysis[1], CTPDC appear to discard the well-known asymptotic van der Waals power law $E = -C_p d^{-p}$ (relating the potential energy E to the interlayer distance d) completely from the Rahaman-Stillinger-Lemberg (RSL2) fitting functions (ϕ^{AB} and ϕ^{AA} , their Equation 1) they use for their Möbius inversion. Instead they replace it by a faster-decaying function that asymptotes to an inverse exponential $E = -K e^{-\kappa d}$. This disregards the long-range component of the van der Waals forces and makes extrapolation from one geometry to another problematic. It leads to qualitative and quantitative discrepancies between their results and theories that do include van der Waals forces.

As a result, their model fails to appropriately treat energy differences between different geometrical arrangements, such as the difference in the per atom energy at equilibrium between stretched graphite and bigraphene. We consider three cases: stretched bulk graphite (where an infinite number of layers are separated equally to d - with energy given by E_{ϕ}^{AB} in Eq. (2) of CTPDC), bigraphene (where two layers are separated to d - given by ϕ^{AB} in Eq. (1) of CTPDC) and exfoliation (where one layer is separated to a distance d from a bulk graphite surface - given by E_{exf} in Eq. (3) of CTPDC). In Table I we show the energy gained by a bigraphene arrangement compared to other arrangements. Results using

CTPDC’s formulae show a significant difference from previous predictions, a direct result of neglecting the van der Waals power laws that contribute energy terms beyond the nearest neighbour layers. Notably, the energetics of exfoliation and graphite stretching are found to be identical in their analysis, as their exponential terms cannot introduce more than second-nearest neighbour contributions.

The poor energetics can be seen most prominently in the case of AA graphite, where insertion of the AA parameters from Table 2 into Equation 1 of CTPDC[1] gives a potential well for $E_{\text{graph-AA}} = E_{\phi}^{AA}$ (from Equation 2 of their work) with a depth of 13800meV/Atom located at $d_0 = 0.076\text{\AA}$. Most other theories find an AA lattice spacing of approximately 3.6Å (see Table 1 of CTPDC). This is almost certainly a result of neglecting the van der Waals power law decay terms from the AA bigraphene potential ϕ^{AA} , leading to a well of depth 328meV/Atom located at $d_0 = 1.29\text{\AA}$ (see inset of Figure 1). This is clearly an unphysical result, and makes portability of the model to new geometries highly dubious.

The neglect of the vdW power law also means that their fit only applies to energies very near contact, and thus cannot be used to predict forces in the important intermediate and outer parts of the binding curve (for example the peak force occurs at $d \approx 3.7\text{\AA}$). This is demonstrated in Figure 1 where their energy results for bulk graphite E^{AB} and bigraphene ϕ^{AA} and ϕ^{AB} are compared with theories[2, 4, 9] that contain appropriate van der Waals power laws. Here the high-level ACFD-RPA[4] is used as a benchmark for AB graphite while the AB bigraphene prediction of Gould, Lebègue and Dobson[9] (GLD), which is guaranteed to reproduce numerous theoretical and experimental properties of graphitic systems, is used as a benchmark for bigraphene in the absence of highly accurate ACFD-RPA results. Apart from the near-contact region of the AB case, their function fit gives substantially quantitatively and qualitatively different results to previous theory, and this discrepancy comes entirely from their neglect of an appropriate van der Waals power law.

In addition to this very fundamental flaw, the paper also contains other misinterpretations of previous theory. Firstly, in their Table I, CTPDC[1] report results obtained using Grimme’s D2 correction[8] on top of either LDA or GGA-PBE. As detailed in the original paper[8], Grimme’s D2 correction is functional dependant via a factor that adjusts the correction to the functional used for the DFT calculations. This factor is obtained by least-squares optimization with respect to a training set of systems in order to reproduce at best the interaction energies and provided[8] for various functionals but not for the LDA. There-

fore in order to correct LDA, one should in principle conduct the same procedure to obtain the corresponding factor, a fact which is not mentioned by CDPBC[1]. It is likely that the authors have used the default parameter provided by the implementation of Grimme’s D2 method[11] in the VASP code[12, 13] which aims at correcting the GGA-PBE functional, but not the LDA, and therefore the LDA/DFT-D2 results in Table I of CTPBC are doubtful. Beside this point, it is generally not advisable to correct results obtained with LDA since this functional, albeit being purely local by construction, gives sometimes a fictitious attraction between van der Waals interacting systems which is even more difficult to correct than a repulsive (or weakly attractive) functional such as GGA-PBE.

Secondly, CTPDC then justify their use of Grimme’s functional by comparing the energetics of stretched graphite with previous random-phase approximation (RPA) theory studies to show that they match the effective power law exponent in a given interlayer distance range. Here they make a fit $y = A/d^{4.2} + C$ and state that this agrees with RPA results by Gould, Simpkins and Dobson[2] (GSD) and Chakarova-Käck *et al.*[14]. However, using the energy curve from GSD yields $y = A'/d^{3.6} + C'$ in the same region, more than half a power of d higher and approaching the asymptotic $y = A''/d^3 + C''$ found in the RPA[2, 4, 5, 15]. The value of 4.2 for the coefficient given in Ref. 4 was found on a range of 3-9Å, including the region of substantial overlap and should thus not be considered asymptotic. The different asymptotic behaviours are illustrated in Figure 2 where we show the results from CTPDC compared with those of GSD, and power law fits to GSD. While their calculations may agree better with Ref. [14], we note that it does not report RPA results at all, at least in the conventional “ACFD-RPA”[16] sense.

Altogether, the neglect of appropriate van der Waals effects by Chen *et al.* means that their energy results are likely to be substantially erroneous, even with good inputs. At best we expect their method to give a crude estimate of the energy of different geometrical arrangements of graphite layers (like exfoliation or cleavage), and even then only in the immediate contact region.

ACKNOWLEDGEMENTS

TG was funded by the Griffith University Areas of Strategic Interest fund.

AUTHOR CONTRIBUTIONS

The corresponding author is TG, who co-wrote the manuscript with SL. TB and SL performed the computational analysis of the *ab initio* calculations. TG did analysis of the fitting functions and semi-analytic work. All authors contributed to discussions.

- [1] Chen, X., Tian, F., Persson, C., Duan, W. & Chen, N. Interlayer interactions in graphites. *Sci. Rep.* **3**, 3046 (2013).
- [2] Gould, T., Simpkins, K. & Dobson, J. F. Theoretical and semiempirical correction to the long-range dispersion power law of stretched graphite. *Phys. Rev. B* **77**, 165134 (2008).
- [3] Gould, T., Gray, E. & Dobson, J. F. van der waals dispersion power laws for cleavage, exfoliation, and stretching in multiscale, layered systems. *Phys. Rev. B* **79**, 113402 (2009).
- [4] Lebègue, S. *et al.* Cohesive properties and asymptotics of the dispersion interaction in graphite by the random phase approximation. *Phys. Rev. Lett.* **105**, 196401 (2010).
- [5] Gould, T., Dobson, J. F. & Lebègue, S. Effects of a finite dirac cone on the dispersion properties of graphite. *Phys. Rev. B* **87**, 165422 (2013).
- [6] Dobson, J. F. & Gould, T. Calculation of dispersion energies. *Journal of Physics: Condensed Matter* **24**, 073201 (2012).
- [7] Gobre, V. V. & Tkatchenko, A. Scaling laws for van der waals interactions in nanostructured materials. *Nat Commun* **4**, – (2013).
- [8] Grimme, S. Semiempirical gga-type density functional constructed with a long-range dispersion correction. *J. Comp. Chem.* **27**, 1787–1799 (2006).
- [9] Gould, T., Lebègue, S. & Dobson, J. F. Dispersion corrections in graphenic systems: a simple and effective model of binding. *Journal of Physics: Condensed Matter* **25**, 445010 (2013).
- [10] Björkman, T., Gulans, A., Krashennnikov, A. V. & Nieminen, R. M. van der waals bonding in layered compounds from advanced density-functional first-principles calculations. *Phys. Rev. Lett.* **108**, 235502 (2012).
- [11] Bucko, T., Hafner, J., Lebègue, S. & Ángyán, J. G. Improved description of the structure of molecular and layered crystals: Ab-initio dft calculations with van der waals corrections. *J. Phys. Chem. A* **114**, 11814 (2010).

- [12] Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **6**, 15–50 (1996).
- [13] Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **59**, 1758–1775 (1999).
- [14] Chakarova-Käck, S. D., Schröder, E., Lundqvist, B. I. & Langreth, D. C. Application of van der waals density functional to an extended system: Adsorption of benzene and naphthalene on graphite. *Phys. Rev. Lett.* **96**, 146107 (2006).
- [15] Dobson, J. F., White, A. & Rubio, A. Asymptotics of the dispersion interaction: analytic benchmarks for van der Waals energy functionals. *Phys. Rev. Lett.* **96**, 073201 (2006).
- [16] Eshuis, H., Bates, J. E. & Furche, F. Electron correlation methods based on the random phase approximation. *Theoretical Chemistry Accounts* **131**, 1–18 (2012).

FIG. 1. Energetic curves from ACFD-RPA[4], compared with those reported by Chen *et al.*[1], Gould, Simpkins and Dobson[2] and Gould, Lebègue and Dobson[9]. Results are included for stretched graphite (lower group of curves) and bigraphene (higher curves).

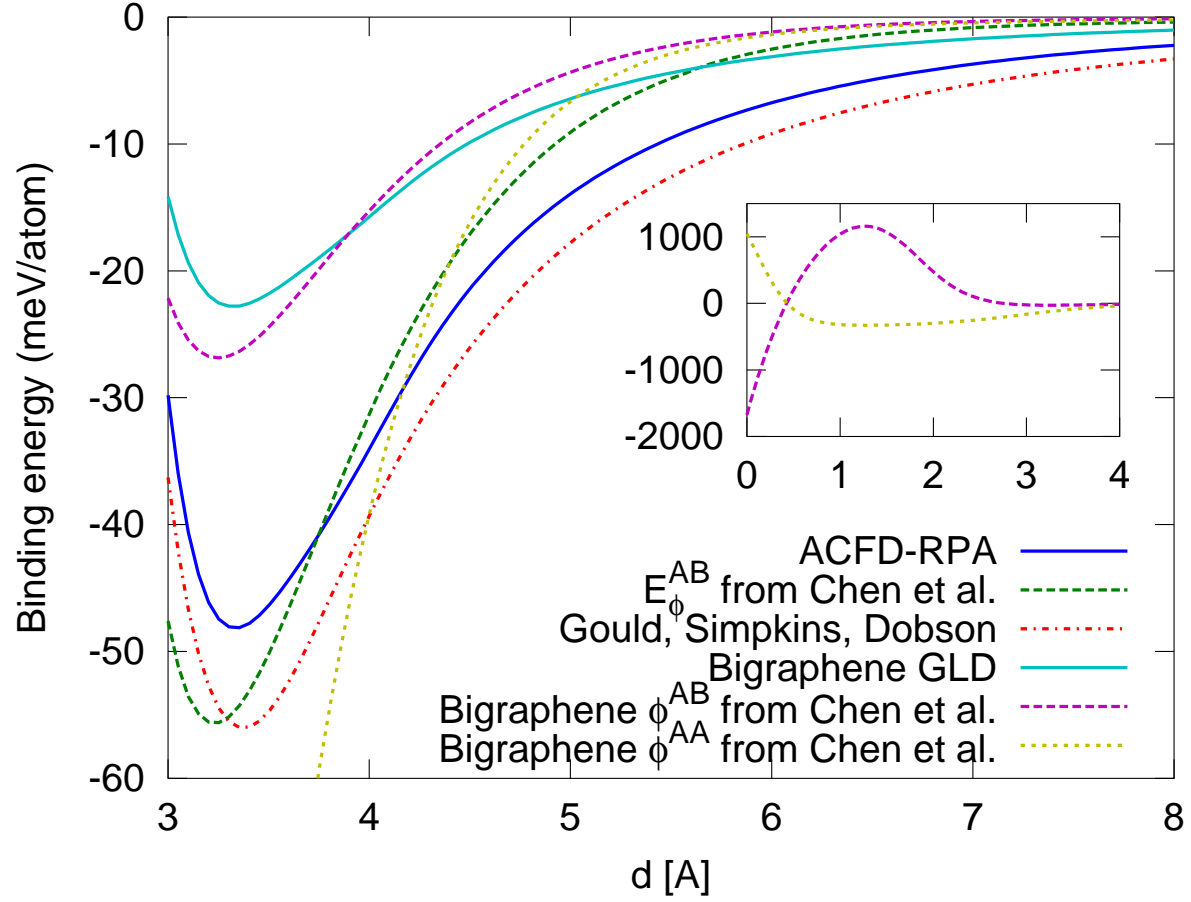


FIG. 2. vdW behaviour as reported by Chen *et al.*[1], and Gould, Simpkins and Dobson[2]. Power law fits to the results of GSD are included for comparison.

